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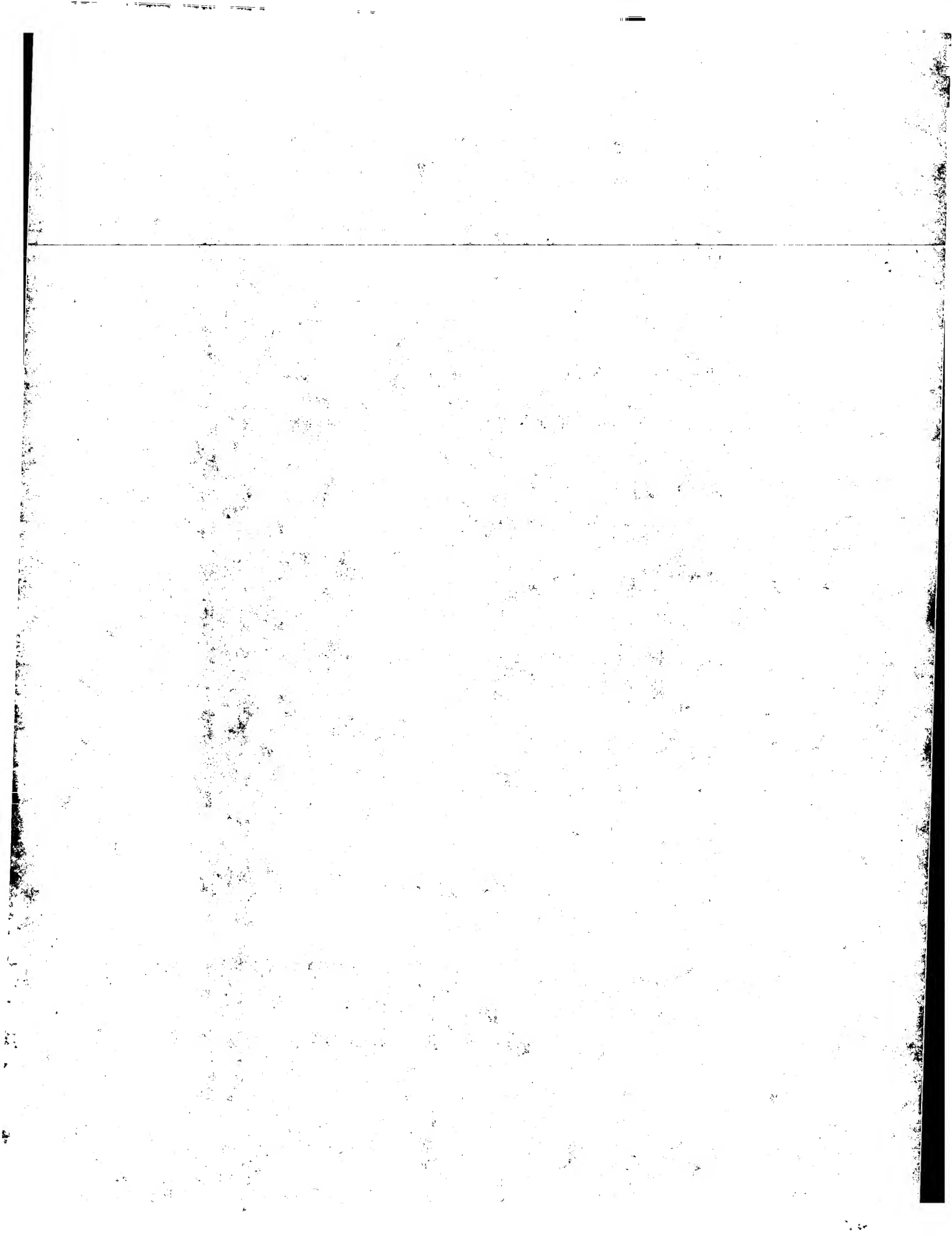
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AMENDED SPECIFICATION

Reprinted as amended under Section 8 of the Patents and Designs Acts, 1907 to 1946.

PATENT SPECIFICATION

575.416



Convention Date (United States of America): Oct. 30, 1942.

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Complete Specification Accepted: Feb. 18, 1946.

(Under Section 6 (1) (a) of the Patents &c. (Emergency) Act, 1939, the proviso to Section 91 (4) of the Patents and Designs Acts, 1907 to 1942 became operative on June 12, 1945).

COMPLETE SPECIFICATION

Process of Modifying the Molecular Structure of Oils and Fats

We, THE PROCTER & GAMBLE COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, located in the Gwynne Building, Sixth and Main Streets, Cincinnati, Ohio, United States of America, assignees of EDDY W. ECKEY, a citizen of the United States of America, residing at 713, Reilly Road, Wyoming, Ohio, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

15 This invention relates to a process for altering the composition of fats and fatty oils which, for convenience, we shall refer to collectively hereinafter in the specification and claims as "fats." More specifically the invention relates to a process for changing the fatty acid composition of glycerides contained in fats.

It is an object of our invention to provide an improved process whereby natural fats may be altered in physical properties.

A further object is to provide a process for changing the fatty acid composition of natural fats.

A special object is to provide a process whereby the combined fatty acids of lower molecular weight in a fat are replaced with fatty acids of higher molecular weight.

In copending application No. 1745/43 filed February 2, 1943, there is described and claimed a method whereby changes in fat composition are effected by subjecting a mixture of the fat and free fatty acid derived from the same fat or other fat to heat treatment under a fractionating column under such temperature and pressure conditions that vaporization of free fatty acids will take place, the fractionat-

ing column being operated so that the more volatile acids vaporized will distill off while the less volatile acids are condensed in the column and returned to the reaction zone, there to react with the glycerides and exchange with more volatile combined fatty acids.

The present process is a further improvement over the art and an improvement over the process covered in the said copending application in that a liquid mixture of a fat and a suitable fatty ester or mixture of same derived from a lower monohydric alcohol (i.e. a monohydric alcohol having less than five carbon atoms) is subjected to heat treatment under a fractionating column under such temperature and pressure conditions that simultaneous molecular rearrangement and vaporization of monohydric alcohol esters take place, the refluxing column being operated so that only the more volatile monohydric alcohol esters and therefore the esters of only the more volatile fatty acids are distilled off while the remainder are condensed in the refluxing column and returned to the reaction vessel wherein further ester interchange takes place.

Methods have heretofore been employed for the interaction of simple mixtures of esters and separation into highest and lowest boiling reaction products, but these methods have not been found applicable to effecting efficient separation of complicated mixtures of esters such as are found in the natural fats and fatty oils.

The process of our invention is particularly applicable to the simultaneous removal of lower boiling acids from and reconstitution of natural fats such as coconut oil, palm kernel oil, and the like which are then particularly valuable because of their high content of C_{12} and C_{14} .

(Price 1/-)

fatty acids. Of course the invention is not limited to this application. Other changes in glyceride composition can be effected by suitable choice of monohydric alcohol ester with which the glyceride is reacted. Molecular rearrangement will be effected whenever the monohydric alcohol ester added to the glyceride is a fatty acid ester having a higher boiling point than the corresponding ester of an acid combined in the glyceride. Thus an oil such as coconut oil containing a rather large proportion of C_8 and C_{10} acids may be converted into a glyceride of higher melting point by mixing the same with methyl stearate, for example, and subjecting to treatment in accordance with the present invention and effecting replacement of at least part of the C_8 and C_{10} acids with stearic acid.

On the other hand, palm oil, which contains a rather large proportion of combined palmitic acid, may be converted into a softer fat by mixing with ethyl oleate and applying the present process so that oleic acid replaces palmitic acid with the formation of ethyl palmitate which is removed by distillation through the fractionating column, any higher boiling ester volatilized such as unreacted ethyl oleate being refluxed and returned to the reaction zone as above set forth in the description of the invention.

Whether or not an ester interchange catalyst should be employed in conjunction with the heat treatment and simultaneous fractional distillation under the fractionating column is dependent upon the final use designed for the product. Conditions may be employed whereby the glyceride alteration and fractional distillation with reflux will take place in the absence of the catalyst, but of course the reaction proceeds considerably slower and therefore a longer time will be necessary to effect the desired degree of modification. In the case of some fats the necessary prolonged treatment at high temperature required when no catalyst is used is injurious to color and may cause considerably polymerization and thermal decomposition. In such instances it is advisable to use a catalyst which will accelerate the reaction so that the fat is subjected to elevated temperature for a minimum length of time. For obvious reasons it is usually preferable to employ a catalyst, but it should be understood that the present invention is not limited to this feature.

The catalysts which may be employed in the type of reaction herein involved are those ester interchange catalysts known in the art such as metal soaps, zinc soap especially being useful. Soaps of aluminum, magnesium and tin may find useful-

ness in some instances. Since it is feasible to conduct the rearrangement and simultaneous fractional distillation under reflux at relatively low temperatures when the volatile alcohol ester interchange process of the present invention is employed, it is also possible to employ small amounts of those catalysts which are especially active in molecular rearrangement processes at low temperature, such as the alkali metal alkoxides preferably of those alcohols employed in the molecular rearrangement process, that is, the alkali metal alkoxides of monohydric alcohols having less than five carbon atoms.

In our study of the process herein described, we have found that for reasons not fully understood, alkali metal alkoxide catalysts lose their effectiveness after the reaction has been allowed to progress for some time, but we have found that whatever the cause may be, it is avoided if, during the molecular rearrangement and simultaneous fractionation under reflux, a vapor of a monohydric alcohol having less than five carbon atoms, preferably but not necessarily, of the monohydric alcohol employed in the preparation of the fatty acid esters is bubbled into the reaction mixture and allowed to escape through the fractionating column. The amount of alcohol used for this purpose does not appear to be critical and for economic reasons we prefer to use small amounts such as two per cent to 10 per cent by weight based on the mixture of fat and monohydric alcohol ester, although a larger amount such as twenty-five per cent may be employed without detrimental effect.

The following example will illustrate a practical method for practicing our process, potassium methoxide catalyst being employed.

EXAMPLE I.

(All parts are by weight.)

Into a still equipped with a suitable fractionating column and adapted to operate under subatmospheric pressure were charged 400 parts refined filtered and dried coconut oil having a saponification value of 255, and 133 parts of dried methyl esters of soybean oil fatty acids, which esters had a saponification value of 191, giving a mixture having a saponification value of 237 (calculated 239). Following the addition of 49.3 parts of a solution of 5.2 parts potassium methoxide in 44.1 parts of methyl alcohol, the charge was heated for about 2—3/4 hours at 25 mm. mercury absolute pressure, the temperature being raised gradually from about 140° C. to 207° C. so as to distill off the more volatile methyl esters formed, while the less volatile esters were condensed in the frac-

tionating column and returned to the still wherein further ester interchange could take place. Throughout the distillation period the charge was agitated by the introduction of methyl alcohol vapors, a total of 40 parts being employed.

According to analyses on the distillate and calculations based thereon, about 90% of the soybean methyl esters were converted by the process to methyl esters of fatty acids of 12 or less carbon atoms, these latter esters being removed in the distillation.

As indicated above, the same process may be conducted without the introduction of alcohol vapors during the rearrangement and distillation and this is true even when alkoxide catalysts are employed. However, although such a process results in an amount of conversion considerably higher than that obtained under conditions heretofore practiced, it will be less than that obtained when the alcohol vapor is introduced.

We have found that the introduction of the alcohol vapor is of advantage in the process when other ester interchange catalysts, such as zinc stearate, are employed. For example, substantially the same result will be obtained if the process of the preceding example is modified to use 2% zinc stearate catalyst (based on the combined weight of coconut oil and soybean methyl ester) at atmospheric pressure, the maximum temperature reached being about 275° C. during the distillation.

Another way in which the reaction may be conducted rapidly and a maximum ester interchange effected is to follow a continuous procedure in which the mixture of fat, methyl ester, alcohol, and catalyst is preheated and immediately introduced into a column still wherein simultaneous rearrangement and volatilization of monohydric alcohol esters are effected. In the column the lower boiling esters formed are vaporized and distilled out of the upper end, while the unvaporized modified glycerides are discharged at the lower end.

We have described above the admixture of methyl stearate with coconut oil and ethyl oleate with palm oil, and in the specific example we have described the treatment of a preformed mixture of coconut oil and the methyl ester of the mixture of fatty acids obtained from soybean oil. It is to be understood that the present invention also embodies that process wherein a part of the fat e.g. coconut oil, to be rearranged is first converted to the monohydric ester *in situ* by mixing with a lower monohydric alcohol in sufficient quantity to form the desired amount of ester and the mixture then treated in

accordance with known ester interchange processes such as by heating the mixture to the boiling point under atmospheric pressure in the presence of a suitable ester interchange catalyst whereby substantially all of the monohydric alcohol is converted into fatty acid ester with the accompanying liberation of free glycerin. At least part of the free glycerin is then removed from the mixture of glyceride and monohydric alcohol ester, which mixture is then subjected to the rearrangement process above described.

The amount of lower alcohol employed will depend on the degree of rearrangement desired and will be the molecular equivalent or slightly in excess thereof of the fatty acid fraction desired to be removed. It will also depend on the oil being used and, as stated before, on the desired degree of rearrangement. In the case of coconut oil, for example, where it is desired to remove those fatty acids of lower molecular weight than lauric (C₁₂) acid and produce glycerides of the higher fatty acids contained in coconut oil, an amount of alcohol slightly in excess of the molecular equivalent necessary to esterify the content of acids below lauric acid in molecular weight will be employed.

It is also possible to use lower monohydric alcohol esters of any single fatty acid having a higher boiling point than corresponding lower alcohol esters producible from the fatty acids in the glycerides, or any mixture of same which may be employed to obtain the desired rearrangement. Methyl, ethyl, propyl, isopropyl and butyl esters may be used in the practice of the invention.

In the practice of that feature of our invention in which the monohydric aliphatic alcohol is introduced into the mixture of glyceride and monohydric alcohol ester and the vapors bubbled therethrough during simultaneous rearrangement and fractional distillation, the alcohol coming over with the distilled esters usually is equal approximately to the quantity introduced. A portion of the alcohol, depending upon the pressure, temperature, and other conditions employed reacts with part of the glyceride to form monohydric fatty acid ester. In some cases it will be advantageous to utilize this effect to the extent of forming all of the monohydric alcohol esters involved in the process simply by passing lower aliphatic monohydric alcohol into the glycerides while being heated in the presence of a suitable ester interchange catalyst under a fractionating column. Applied to coconut oil, this method may be used to remove most of the lower boiling fatty acids, C₆-C₁₀, from the mixed glycerides of the oil. The fol-

lowing example will illustrate this process in more detail, it being understood, of course, that the example is merely illustrative and that we are not limited thereto:—

EXAMPLE II.

A mixture of 500 parts coconut oil and 10 parts of zinc stearate was heated to 260°—270° C. at one atmosphere pressure in a still provided with a fractionating column while methyl alcohol was passed through the charge. For about 8 hours thereafter the temperature was maintained at 260°—270° C. and methyl alcohol was introduced at an average rate of about 30 parts by weight per hour. Fractions of distillate were collected from time to time and treated to separate methyl ester from methyl alcohol. Methyl esters totaling about 13% of the charge were distilled over. The combined ester distillate had a saponification value of 309. The product remaining in the still contained about 25% methyl esters (b.p. 150—175° C. at 25 mm. Hg.) which were removed by distillation under vacuum. These esters had a saponification value of 245. The residual glyceride mixture had a saponification value of 236 as compared with 255 for the original oil.

The fats which respond to our method of treatment and which undergo radical change in composition and properties when subjected thereto are the natural triglyceride fats and oils and mixtures of same, including animal, vegetable and marine fats and oils such as tallow, cottonseed oil, coconut oil, palm oil, whale oil, fish oil, etc.

The temperature at which our process may be conducted will vary somewhat depending on the mixture of fat and monohydric alcohol esters being subjected to treatment. Of course it is essential that the temperatures employed be sufficiently high to vaporize the monohydric alcohol ester under the existing pressure conditions and sufficiently high to bring about the simultaneous exchange of fatty acid in the triglyceride. Ordinarily the pressure conditions should be adjusted either above or below atmospheric pressure so that the temperature at which the esters boil will be sufficiently high to effect simultaneous rearrangement and vaporization without undesired thermal decomposition. Temperatures from 150° C. to 275° C. have been found satisfactory.

Oils and fats modified according to the invention are useful, for example, in the manufacture of edible products and also in the soap and paint industries.

We are aware of Specification No. 249,916 which describes the modification of the properties of fats and oils by cata-

lytic heat-treatment with a lower monohydric alcohol ester of a fatty acid. According to Example 3 of that specification, coconut oil and ethyl stearate are stirred together at a temperature of 250° C. under a slow current of carbon dioxide which is accelerated after 1½ hours of heating so as to distil off the more volatile ethyl esters of the coconut oil fatty acids which had been formed by the reaction. The process of the present invention is distinguished from this process in that the rearrangement reaction in the present process proceeds simultaneously with the vaporizing of at least part of the monohydric alcohol ester present in the mixture, and that the vaporized esters are fractionated and the less volatile fraction is returned to the reaction zone to permit further reaction with the glycerides, thus rendering it possible to obtain a considerably more extensive change in the glyceride structure.

We are aware of Patent No. 590,951 which claims a method of treating glyceride oils containing glycerides of relatively low molecular weight fatty acids, which comprises subjecting said glyceride oils to the vapors of lower alkylesters of higher molecular weight fatty acids so as to replace the lower molecular weight fatty acids in said glycerides by the higher molecular weight acids. This is distinguished from the process claimed in the present specification which relates only to a reaction in the liquid phase.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for altering the composition of a fat which comprises subjecting a liquid mixture of a fat and a fatty acid ester of a monohydric aliphatic alcohol having less than five carbon atoms per molecule to a temperature at which molecular change in the glyceride will take place, simultaneously vaporizing at least part of the monohydric alcohol ester present in the mixture, fractionating the vaporized esters, returning the less volatile fraction to the reaction zone to permit further reaction with the glycerides, and removing the more volatile fraction.

2. A process for altering the composition of a fat, which comprises subjecting a liquid mixture of a fat, a molecular rearrangement catalyst, and a saturated or unsaturated fatty acid ester of a monohydric aliphatic alcohol having less than five carbon atoms per molecule, to a temperature at which ester interchange and volatilization of monohydric alcohol ester will take place without substantial thermal

- decomposition, the monohydric alcohol ester admixed with the fat having a higher boiling point than an ester of the same alcohol and a fatty acid combined in the glyceride, passing the vaporized esters into a fractionating column, condensing the higher boiling esters and returning same to the reaction zone, and permitting the lower boiling esters to pass through said column.
3. A process as claimed in claim 1 or 2 applied to a mixture of a glyceride fat, and esters of fatty acids of the same fat or other fat and a monohydric alcohol having less than five carbon atoms.
4. A process as claimed in claim 1 or 2 applied to a mixture of coconut oil and esters of fatty acids of coconut oil and a monohydric aliphatic alcohol having less than five carbon atoms per molecule.
5. A process as claimed in any of the preceding claims in which an alkali metal alkoxide is employed as an ester interchange catalyst.
6. A process as claimed in any of claims 1 to 4 in which a metal soap ester interchange catalyst is employed.
7. A process as claimed in any of the preceding claims in which vapor of an aliphatic monohydric alcohol having less than five carbon atoms is passed through the reaction mix during the reaction and vaporization.
8. A process as claimed in any of the preceding claims in which the fatty acid ester is produced in the mixture by conversion from part of the glycerides by alcoholysis treatment with the monohydric aliphatic alcohol, at least part of the liberated glycerin being removed.
9. A process for altering the composition of coconut oil substantially as described in Example 1 or 2.

Dated this 14th day of July, 1943.

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